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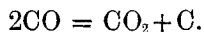
ON THE DECOMPOSITION OF CARBON MONOXIDE IN THE PRESENCE OF REDUCED NICKEL.

(Preliminary Report)

By Shinkichi HORIBA and Taikei RI.

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As one of the most simple catalytic reactions, we may cite the decomposition of carbon monoxide in the presence of reduced nickel:



Although many studies of this reaction have been given in the literature, still a more comprehensive investigation of such a simple catalytic reaction is to be desired, for it would, in the writers' opinion, contribute some important materials to facilitate the theoretical studies of contact catalysis, which is one of the most interesting problems in physical chemistry at the present time.

Since this catalytic reaction had been found by Ste.-Claire Deville⁽¹⁾ in 1863, it was studied by many investigators, but their modes of investigation can, in general, be divided into two classes; namely, the first is related to chemical statics (equilibrium), and the other to the kinetics of the reaction. The number of report belonging to the former class is very great,⁽²⁾ since the investigation of the equilibrium of this reaction has much value in technics, while that of the latter class is inconsiderable.⁽³⁾ So far as the present writers know, there is no investigation of this reaction which is simultaneously studied from the two view points of reaction statics and of kinetics. The writers have, therefore, constructed an improved apparatus for the measurement of the reaction velocities as well as of the equilibrium, in the hope of elucidating the relationship that may be established between the reaction statics and the reaction kinetics and also to deduce the mechanism of the nickel catalyst. In the present paper, as a preliminary note, only the description of the apparatus constructed and some results of experiments will be given.

(1) Ste.-Claire Deville, *Compt. rend.*, **56** (1863), 729.

(2) Boudouard, *Ann. chim. phys.*, [7], **24** (1901), 5; Max Mayer, "Habilitationsschrift Karlsruhe," (1908); Read and Wheeler, *J. Chem. Soc.*, **97** (1910), 2181; *ibid.*, **99** (1911), 1140; Arndt and Schraube, Dissertation Charlottenburg (1911); Falcke, *Z. Elektrochem.*, **27** (1921), 268; Jellinek and Dithem, *Z. anorg. allgem. Chem.*, **124** (1922), 203; Falcke and Fischer, *Z. Elektrochem.*, **32** (1926), 194; Falcke, *ibid.*, **33** (1927), 1; Alfred Stansfield, *Trans. Am. Elektrochem. Soc.*, **51** (1927), 5.

(3) Schenk and Zimmermann, *Ber.*, **36** (1903), 1231 & 3663; Smits and Wolff, *Z. physik. Chem.*, **45** (1903), 199; J. Cleminson and H.V.A. Briscoe, *J. Chem. Soc.*, (1926), 2148.

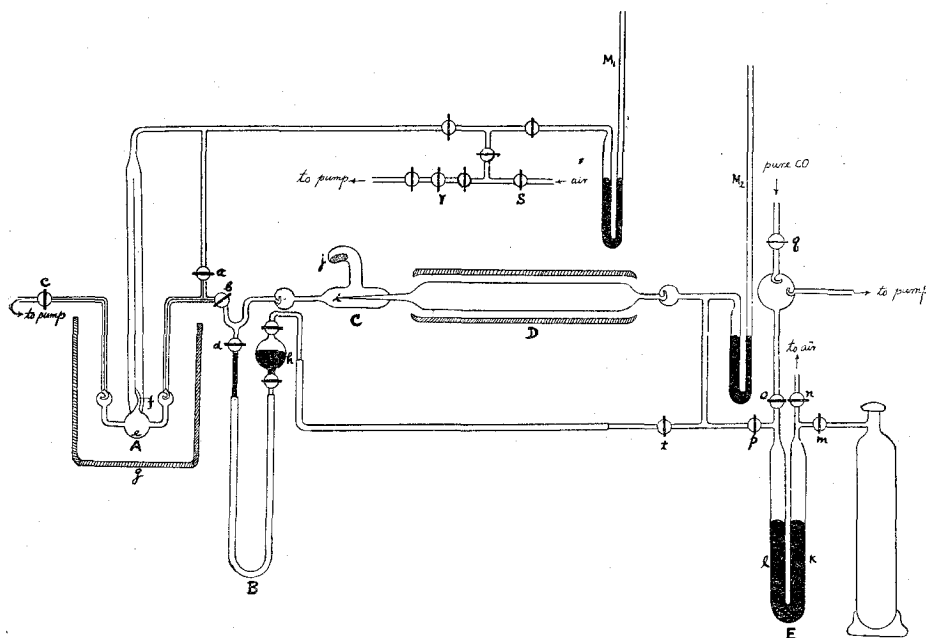


Fig. 1.

Apparatus of the Measurements. The apparatus constructed is mainly divided into five parts, as represented by A, B, C, D and E in Fig. 1. A is the reaction vessel (made of Pyrex glass) provided with a spring manometer *f* and with two capillary tubes which are furnished with cocks *a*, *b* and *c* and when these cocks are closed the internal volume of this reaction vessel is about 30 c.c. The catalyst was placed into the part *e* of the vessel. The cock *b* is a specially made one, 2.4 cm. in diameter and 12 cm. in length, two sides of which were sealed by means of mercury from the atmosphere. In this cock, the least possible modicum of grease was applied for the sake of lubrication on two sides of it, but absolutely none in the middle part of the cock; the employment of such a cock is of vast importance in the present experiment, otherwise a minute trace of grease may enter into the reaction vessel accompanying the stream of carbon monoxide, when the latter was charged into the evacuated vessel A. The bath *g* is made up of a melted mixture of sodium and potassium nitrates in an equimolecular proportion, provided with two glass rods for stirring.

B is that part of the apparatus intended to secure the perfect sealing of the cock *b* to prevent any leaking of gas through the nongreased portion of *b*, and this sealing was performed by shutting up the Y-formed glass tube with mercury, by bringing up the mercury reservoir *h*. To prevent the

contamination of the mercury by the grease, the other cock *d*, which was constructed in the same form as *b*, was employed.

C is the apparatus for charging the reaction vessel with the gas, and it was also used merely to prevent the entering of the grease into the reaction vessel. The glass tube *i* is drawn out at one end into a fine point and sealed, and *j* is a piece of soft iron covered with glass. In charging the reaction vessel with the gas from the preheater D, into which the gas had previously been poured, the soft iron falls on the end of the glass tube *i* by means of a magnet and breaks it: as a consequence the gas streams into the evacuated reaction vessel through the Y-formed tube and cock *b*.

D is the preheater of the reacting gas before it is poured into the reaction vessel, and was used for the purpose of equalizing the temperature of the gas and that of the reaction vessel A; for heating D, an electric furnace was used, and its temperature was measured by a platinum-platinum-rhodium thermocouple.

E is the pump to raise the pressure of the gas in the preheater to the desired amount. Its height is about 90 cm. and was filled with mercury up to the height of 45 cm. For supplying the pressure to this pump a CO₂ bomb was used as shown in the figure.

Materials. The catalyst used was prepared by ignition of pure nickel nitrate Ni(NO₃)₂·6H₂O (Kahlbaum, Co free) in a crucible, subjected to a red heat during one day, and then the NiO thus prepared (about 10 gr.) was introduced into the reaction vessel A and reduced by electrolytic hydrogen (purified) at a temperature of 280°C.

Carbon monoxide was prepared by dropping pure formic acid on heated sulphuric acid at 100°C. and this was purified by passing three bottles each of conc. KOH solution and pyrogallol solution, two bottles of conc. H₂SO₄ and then a P₂O₅ tube, and it was found that the purity of the thus prepared carbon monoxide was 100%.

The Method of the Measurements. The reaction vessel was heated in the nitrate bath *g* at the desired temperature and the whole apparatus was evacuated with a Cenco Hyvac pump, leaving open all the cocks except *m*, *n*, *q* and *s*, until the Geisler tube, which was attached to the pump, showed fluorescence. Then the cocks *c* and *d* were closed and through the cock *q* purified carbon monoxide was introduced into the pump E and preheater D. Next, with the aid of pump E, carbon monoxide was compressed into the preheater, which was heated to the same temperature as the reaction vessel, at the desired pressure. The pressure of D before pouring it into the reaction vessel was read by means of the mercury manometer M₂; from this reading of the pressure, the pressure, which would be exerted by the gas in the reaction vessel after being charged, could be expected. Now the

soft iron piece above mentioned has made fallen and broken the end of the narrow tube *i*, thus the gas streamed into the reaction vessel A. When all the systems had reached an equilibrium of pressure, the cock *d* was opened, then the mercury ran from the reservoir, which was held previously at a suitable height, into the Y-formed tube and sealed this part. The cocks *a*, *b* and *d*, then, were quickly closed, the pressure of the reaction vessel at the initial time being read by the manometer *M*₁; the whole time required in this charging process of the gas was only about 10 seconds. The gas thus enclosed within the reaction vessel of constant volume by the above procedure decomposes to CO₂ and C in the presence of the nickel catalyst. During the progress of the reaction, the pressure change of the reaction vessel is easily indicated by the spring manometer. Adjusting the outer pressure of the spring by means of the cocks *r* and *s* and keeping the pointer of the spring manometer in the zero position, the pressure of the reaction vessel at any time was measured. By reading the pressure from time to time in this way, the decomposition velocity of the gas was determined.

The Experimental Results. The results of the four series of experiments in the vicinity of 230°C., applying the same catalyst, were as follows:

TABLE 1.
(at 232.5°C.)

Time. (min.)	Press. (mm.)	2.303 <i>k</i> (time in min.)
0.00	270.4	
2.42	256.2	0.0204
3.73	243.1	0.0264
5.88	231.0	0.0256
8.23	219.6	0.0249
11.27	207.2	0.0240
12.90	201.7	0.0238
14.18	197.7	0.0238
15.10	194.1	0.0240
17.56	190.6	0.0222
18.63	187.0	0.0224
20.18	183.7	0.0222
22.08	178.5	0.0225
25.69	175.8	0.0204
(remained constant for about 10 min. and then increased very slowly.)		

TABLE 2.
(at 230°C.)

Time. (min.)	Press. (mm.)	2.303 <i>k</i> (time in min.)
0.00	272.7	
1.00	255.1	0.0607
2.87	242.4	0.0383
4.75	235.4	0.0295
7.00	225.1	0.0268
8.70	221.1	0.0239
9.90	217.3	0.0230
11.63	211.9	0.0222
13.10	207.8	0.0215
14.50	202.1	0.0219
16.95	197.2	0.0207
19.27	192.0	0.0203
21.68	186.4	0.0201
24.30	179.9	0.0204
26.75	174.9	0.0205
30.10	170.6	0.0200
32.72	167.9	0.0195
38.22	162.8	0.0187
(tended to increase; after about 40 min. increased to 178.0 mm.)		

TABLE 3.
(at 233.5°C.)

Time. (min.)	Press. (mm.)	2.303 <i>k</i> (time in min.)
0.00	272.0	
1.05	253.9	0.0592
2.53	242.7	0.0423
3.95	232.3	0.0379
5.55	224.7	0.0333
7.18	216.8	0.0312
9.12	209.1	0.0296
11.40	200.1	0.0287
13.43	196.8	0.0260
15.03	190.8	0.0258
16.80	185.6	0.0261
18.88	179.2	0.0264
21.58	174.1	0.0257
23.73	168.6	0.0262
26.72	165.0	0.0252
(tended to increase; after about 40 min. increased to 176.2 mm.)		

TABLE 4.
(at 231.5°C.)

Time. (min.)	Press. (mm.)	$2.303 k$ (time in min.)
0.00	253.3	
1.08	239.1	0.0472
2.40	229.0	0.0385
3.83	221.1	0.0333
5.15	215.1	0.0301
6.90	206.5	0.0290
9.07	199.4	0.0265
11.72	191.0	0.0250
15.20	182.3	0.0235
17.93	177.8	0.0219
20.60	172.3	0.0215
23.82	167.1	0.0209
27.53	162.2	0.0201
31.57	155.8	0.0202
36.95	152.8	0.0185
(remained constant for 8 min.; after 35 min. in- creased to 163.3 mm.)		

The values of k in the third column were obtained by the application of the ordinary monomolecular reaction formula,

$$k = \frac{1}{t} \ln \frac{p_0}{2p_t - p_0},$$

where p_0 and p_t denote the initial pressure and the pressure of time t respectively.

In every experiment, the constancy of the reaction constant, after about 15 minutes, is quite good, and it shows that the decomposition of carbon monoxide is monomolecular. Now what about the rapid decreasing of the pressure in the initial period of the reaction? The writers hold the opinion that it might be mainly due to the adsorption of carbon monoxide on reduced nickel. In fact, if we take the adsorption formula⁽¹⁾

$$k' = \frac{1}{t} \ln \frac{A}{A-x},$$

where A denotes the total amount adsorbed when equilibrium is attained, and x the amount adsorbed in the time t , we have approximate constant values about the adsorption velocity constant k' , after choosing suitable values in A from the data of the above experiments, for examples:

(1) Blythswood and Allen, *Phil. Mag.*, 10 (1905), 497.

TABLE 5.

Time. (min.)	$x (=p_0-p_t)$	k' (time in min.)
(from Table 2)		
0.00	0	
1.00	17.6	0.1245
2.87	30.3	0.0848
4.75	37.3	0.0688
7.00	47.6	0.0695
8.70	51.6	0.0656
9.90	55.4	0.0676
11.63	60.8	0.0738
13.10	64.9	0.0834
where $A=272.7-202.1=70.6$ mm.		
(from Table 4)		
0.00	0.	
1.08	14.2	0.0893
2.40	24.3	0.0758
3.83	32.2	0.0686
5.15	38.2	0.0650
6.90	46.8	0.0732
9.07	53.9	0.0682
11.72	62.3	0.0780
where $A=253.3-182.3=71.0$ mm.		

We may say, it is not at all improbable that reduced nickel has such degree of adsorptive power towards carbon monoxide even at that temperature, if we noticed remarkable adsorptive power of it at low temperature. About the latter, the writers have already carried out experiments, which will be published in the near future.

As seen in the present experiments, the decomposition of carbon monoxide is not complete at those temperatures. This result contradicts the prediction from the studies of chemical statics of this reaction, which had been carried out by many investigators, and it requires further studies to clear up reason for this.

As shown in the tables 1-4, in every experiment, the pressure at the end of the reaction tends to increase, even if this velocity of increasing pressure is exceedingly small compared to that of the decomposition of the gas. The cause of this increasing of the pressure is not yet clear. The

writers hold the opinion that it depends upon the reaction between carbon dioxide or carbon monoxide and hydrogen; the latter would be brought into the system by the adsorption of the catalyst when it was prepared. The experiments in connection with this problem are now proceeding.

Even the some difficulties as above described in this reaction still remain, it is quite certain that the decomposition of carbon monoxide in the presence of a nickel catalyst is monomolecular and it may, therefore; be explained by Langmuir's theory of heterogeneous reaction. But this theoretical discussion will be left until a more comprehensive examination is concluded.

Summary.

An improved apparatus for the investigation of contact catalysis was described.

The decomposition of carbon monoxide in the presence of reduced nickel is a monomolecular reaction in the vicinity of 230°C.

December 1927.

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Kyoto.
